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Description

The present invention relates to a cement admixture and a cement composition having the fluidity improved. Particularly, it relates to a cement admixture and a cement composition useful for various applications including applications as concrete materials having high density and excellent durability, as repair materials, as floor materials, as water preventing materials, as adhesive materials and as building materials.

In recent years, the durability of reinforced concrete structures has been problematic, and it has been desired to develop reliable repair materials.

Namely, with respect to concrete structures, there has been a problem that the durability of concrete deteriorates due to the following reasons:

- (1) Due to carbonation caused by the penetration of carbon dioxide gas from the surface of the concrete, the pH of the interior of the concrete lowers, whereby the steel bar (reinforced) will be corroded.
- (2) The steel bar will be corroded by the penetration of chlorine ions from the exterior of the concrete to the interior thereof.
- (3) Silicious mineral in the aggregate undergoes an expansion reaction with an alkali eluted from the cement.
- (4) When sea sand is used as the aggregate, the steel bar will be corroded.

To solve such problems, particularly the problems identified in items (1) and (2), a repair technique has been studied which comprises scraping off the concrete from the corroded portion of the steel bar, then applying rust-preventing treatment to the steel bar and then injecting a repair polymer modified cement employing various polymers such as polymers of acrylate type, vinyl acetate type, vinylidene chloride type, vinyl chloride type, styrene-butadiene type and chloroprene type, to improve the bonding to the concrete.

The reasons for employing such polymers are:

- ① To improve the adhesive strength to the old concrete;
- ② To prevent cracking of thin layer repair portions; and
- ③ To improve the flexural strength of the repair mortar and to impart resiliency.

Japanese Examined Patent Publication No. 33054/1972 discloses a modified cement product having an ethylenevinyl acetate copolymer latex with a vinyl acetate component content of from 60 to 90 parts by weight incorporated to cement in an amount of from 2 to 40 parts by weight as solid content.

Further, Japanese Unexamined Patent Publication No. 85444/1980 discloses a cement product having a vinyl acetate-ethylene-acrylate copolymer latex (50-95/5-49.5/0.5-45 parts by weight) incorporated to cement in an amount of from 1 to 30 parts by weight as solid content.

Japanese Unexamined Patent publication No. 61338/1990 discloses a cement admixture comprising an ethylene-vinyl acetate copolymer latex having an average particle size of from 0.2 to 0.5 μm and an ethylene content of from 10 to 25 parts by weight, wherein as an emulsion stabilizer, a certain specific colloid and a certain specific surfactant are employed.

However, to secure the fluidity with such conventional cements containing various polymers, it was necessary to adjust the water/cement ratio at a high level, and the structure of the resulting concrete tended to be coarse, whereby the permeation rate of noxious gas or chlorine ions was high, and it was difficult to sufficiently prevent the corrosion of the steel bar located in the interior of the concrete.

Further, in order to increase the durability of concrete, it has been known to employ a water reducing agent as a cement admixture to reduce the water/cement ratio without impairing the fluidity, to prevent the permeation of noxious gas or chlorine ions and to improve the durability of the concrete. Namely, the water reducing agent is a cement admixture to reduce the water/cement ratio without impairing the fluidity, to prevent the permeation of noxious gas or chlorine ions and to improve the durability of concrete. For example, water reducing agents comprising a salt of a naphthalene sulfonic acid formaldehyde condensation product, a salt of a melamine sulfonic acid formaldehyde condensation product, a high molecular weight lignin sulfonate or a polycarboxylate, as the main component are used. Among them, it is particularly preferred to employ a salt of a melamine sulfonic acid formaldehyde condensation product having a high condensation degree.

However, when such water reducing agents are used, cracking is likely to occur, since the water/cement ratio becomes low. If cracking occurs, the durability will be poor. Therefore, it has been desired to provide a concrete which is hardly susceptible to cracking.

Under these circumstances, it has been studied to incorporate to a repair cement a polymer latex which is capable of providing cracking resistance and adequate adhesive strength to concrete. However, it has been very difficult to secure the fluidity while incorporating a water reducing agent to reduce the

The present inventors have conducted various studies to solve the above problems and as a result, have found it possible to provide a polymer modified cement composition having the fluidity improved, by using a certain specific copolymer latex and a water reducing agent having a specific composition. The present invention has been accomplished on the basis of this discovery.

Thus, the present invention provides a cement admixture comprising a polymer latex, ultrafine particles having an average particle size smaller by at least one order of magnitude than the average particle size of the cement material, and a water-reducing agent as effective components, wherein the polymer latex comprises a copolymer of monomers comprising ethylene, vinyl acetate and acrylic ester and an emulsion stabilizer, wherein said emulsion stabilizer is a surfactant in the absence of a colloid.

Further, the present invention provides a polymer modified cement composition comprising the above cement admixture and cement as the main components.

Now, the present invention will be described in detail with reference to the preferred embodiments.

The copolymer latex to be used in the present invention contains a large amount of water. Therefore, it is possible to reduce the water content by employing a powder obtained by drying such copolymer latex.

Now, the copolymer latex as one of the essential constituents of the present invention will be described. The copolymer latex of the present invention comprises a copolymer of monomers comprising ethylene, vinyl acetate and an acrylic ester, and an emulsion stabilizer. The copolymer is preferably a copolymer of monomers comprising from 3 to 25 parts by weight of ethylene, from 2 to 60 parts by weight of vinyl acetate, from 25 to 85 parts by weight of an acrylic ester and from 0 to 10 parts by weight of other copolymerizable monomers.

If the ethylene content is less than 3 parts by weight, if the vinyl acetate content is less than 2 parts by weight, if the acrylic ester content is less than 25 parts by weight, or if the vinyl acetate content exceeds 60 parts by weight, when such a copolymer latex is admixed to cement, the fluidity tends to be poor, and the operation efficiency tends to be poor. Further, it tends to be difficult to obtain an adequate cracking resistance of the solidified cement product. On the other hand, if the ethylene content exceeds 25 parts by weight, or if the acrylic ester content exceeds 85 parts by weight, the cohesion of the polymer tends to be low, and when it is admixed with cement, the adhesive strength to the substrate tends to be low, such being undesirable.

As the acrylic ester to be used in the present invention, a soft polymer capable of imparting flexibility to improve the cracking resistance is preferred. Namely, it is preferred to employ an acrylic ester having a glass transition temperature (T_g) of $T_g \leq -20^\circ\text{C}$, such as ethyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate or 2-ethylhexyl acrylic ester. These acrylates can be used alone or in combination as a mixture of two or more.

For the preparation of the polymer latex of the present invention, conventional methods including batch polymerization methods and continuous polymerization methods may be employed.

For the preparation of a polymer latex by emulsion polymerization, it is common to employ as an emulsion stabilizer a colloid such as a polyvinyl alcohol (PVA) or hydroxyethyl cellulose (HEC) alone or together with a surfactant. However, as in the present invention, when a water reducing agent is to be incorporated, particularly, with a cement containing a polymer having the water/cement ratio reduced, there will be an adverse effect to the fluidity if such a colloid is used as an emulsion stabilizer. The detailed mechanism causing such an adverse effect to the fluidity is not clearly understood. However, it is believed that the thickening effect due to the formation of a complex of such a colloid with various salts used as water reducing agents, may be a cause.

The colloid causing an adverse effect to the fluidity includes cellulose derivatives such as carboxymethyl cellulose (CMC), methyl cellulose (MC), hydroxyethyl cellulose and hydroxypropyl cellulose (HPC), guar gum, gum arabic, acacia gum, tragacanth gum, tamarind seeds, gelatin, polyacrylamide and polyvinyl alcohol.

In the present invention, as the emulsion stabilizer, a surfactant is employed. In addition, a water-soluble oligomer formed during the polymerization process also serves as an emulsion stabilizer. Therefore, it is also effective to use a polymerization initiator at a high concentration.

The surfactant to be used as the emulsion stabilizer includes anionic, cationic and nonionic surfactants.

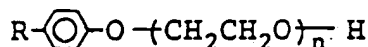
Anionic surfactants include sodium vinyl sulfonate, sodium styrene sulfonate, sodium 2-sulfoethyl methacrylate, sodium allyl alkyl sulfosuccinate, a sodium salt of a sulfuric acid ester of a higher alcohol and an ammonium salt of a polyoxyethylene alkylphenylether sulfate.

Cationic surfactants include 2-aminoethyl methacrylate hydrochloride and 2-hydroxy-3-trimethylaminopropyl methacrylate chloride.

Nonionic surfactants include a polyoxyethylene condensation product, a polyoxyethylene polyox-

It is particularly preferred to employ a nonionic surfactant of the formula $\text{HO}(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_5\text{O})_b(\text{C}_2\text{H}_4\text{O})_c\text{H}$ or

5



wherein R is a C_6 - C_{18} alkyl group, and having a HLB of from 14 to 19.

The surfactant is used usually in an amount of from 0.1 to 10 parts by weight relative to 100 parts by weight of the vinyl acetate and acrylic ester components in the copolymer latex. If the surfactant is less than 0.1 part by weight, it is difficult to conduct emulsion polymerization. On the other hand, if it exceeds 10 parts by weight, the surfactant tends to adversely affect the water resistance and the alkaline resistance.

As the polymerization initiator, a persulfate such as potassium persulfate, hydrogen peroxide, or various organic peroxides may be employed. In the case of a redox initiation system, sodium formaldehyde sulfoxylate or the like may further be used in combination as a reducing substance.

The copolymer in the copolymer latex to be used in the present invention may further contain one or more copolymerizable monomers in an amount not to interfere with the effects of the present invention i.e. usually up to 10 parts by weight.

Such comonomers include a vinyl cyanide monomer such as acrylonitrile or methacrylonitrile, an unsaturated carboxylic acid monomer such as acrylic acid, methacrylic acid, itaconic acid or crotonic acid, a methacrylate monomer such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate or glycidyl methacrylate, a vinyl ether monomer such as methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether or phenyl vinyl ether, an amide monomer such as acrylamide or methacrylamide, a maleimide monomer such as maleimide, N-methylmaleimide, N-ethylmaleimide, N-propylmaleimide, N-phenylmaleimide or N-toluylmaleimide, a halogenated olefin monomer such as vinyl chloride or vinylidene chloride, and a polyfunctional vinyl monomer such as divinyl benzene, ethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butylene glycol dimethacrylate, propylene glycol dimethacrylate, polyethylene glycol dimethacrylate, polypropylene glycol dimethacrylate, ethylene glycol diacrylate, polyethylene glycol diacrylate, triallyl cyanurate, triallyl isocyanurate, trimethylol propane trimethacrylate, allyl acrylate or allyl methacrylate.

Further, conventional additives such as a pH controlling agent (buffer), a defoaming agent and an antiseptics may be incorporated as the case requires.

The size of the particles in the copolymer latex thus obtained is preferably within a range of from 0.05 to 5 μm .

The copolymer latex of the present invention thus obtained is preferably used in an amount of from 4 to 150 parts by weight as solid content relative to 100 parts by weight of cement. If the amount is less than 4 parts by weight as solid content, no adequate adhesive strength will be obtained. On the other hand, even if it is added beyond 150 parts by weight as solid content, no further increase of the adhesive strength will be obtained, and the abrasion resistance or strength of the surface and the weather resistance tend to be inadequate.

The water reducing agent and superplasticizer to be used in the present invention may be at least one member selected from the group consisting of a salt of a naphthalene sulfonic acid formaldehyde condensation product, a salt of an alkyl-naphthalene sulfonic acid formaldehyde condensation product, a salt of a melamine sulfonic acid formaldehyde condensation product, a lignin sulfonate, a high molecular weight lignin sulfonate, a polycarboxylate and a polystyrene sulfonate. From the viewpoint of e.g. the solidification time, it is particularly preferred to employ a salt of a melamine sulfonic acid formaldehyde condensation product with a high condensation degree.

As the salt of a melamine sulfonic acid formaldehyde condensation product to be used in the present invention, "Seakament" trade name, manufactured by Nippon Seika K.K. or "Melment" trade name, manufactured by Showa Denko K.K., may be mentioned.

The naphthalene sulfonic acid formaldehyde condensation product or the alkyl-naphthalene sulfonic acid formaldehyde condensation product is used usually in the form of an alkali metal salt, an alkaline earth metal salt or an ammonium salt. As such a salt, sodium β -naphthalene sulfonate or potassium β -naphthalene sulfonate may be mentioned. As commercial products, "Denka FT-500" trade name, manufactured by Denki Kagaku Kogyo K.K. and "Selfro-110P" trade name, manufactured by Daiichi Kogyo Seiyaku K.K., may be mentioned.

As the lignin sulfonate, "Sanflow K" trade name, manufactured by Sanyo Kokusaku Pulp Co., Ltd. or

As the lignin sulfonate having high molecular weight, "Ultragin" trade name, manufactured by Bolgard Company, may be mentioned. As the polycarboxylate, there may be mentioned "600S" trade name, manufactured by Nippon Shokubai Kagaku Kogyo K.K. obtained by reacting an alkylene amine and/or an alkylene oxide to a carboxyl group-containing polymer for addition reaction, "Work 500" or "M-10" trade name, manufactured by Nihon Zeon K.K. which is a hydrolyzate of a product obtained by copolymerizing an olefin with an ethylenically unsaturated dicarboxylic anhydride, and a hydrolyzate of a copolymer of an olefin with maleic anhydride or a copolymer of styrene or other copolymerizable monomer with maleic anhydride, which is a gradual releasing type exhibiting fluidity by being gradually hydrolyzed by an alkali from the cement in the form of an anhydride.

The water reducing agent and superplasticizer of the present invention may be added in a powder form. However, it is of course possible to add it in the form of a liquid.

The water reducing agent and superplasticizer is used usually in an amount of from 0.15 to 5 parts by weight relative to 100 parts by weight of cement. Also in the present invention, it is preferred to add it in a similar amount, more preferably from 0.15 to 4 parts by weight, although the amount varies depending upon the water/cement ratio. If the amount is less than 0.15 part by weight, it tends to be difficult to obtain adequate fluidity, and if it exceeds 5 parts by weight, no further improvement in the fluidity will be obtained.

In the cement admixture of the present invention, the ratio of the solid content of the copolymer latex to the water reducing agent and superplasticizer is preferably within a range of from 98:2 to 10:90 by weight.

The amount of water to be incorporated should better be as low as possible relative to cement from the viewpoint of the object of the present invention.

Here, cement is a material composed essentially of a cement material.

As the cement material, it is common to employ various Portland cements such as normal Portland cement, high early strength Portland cement, super high early strength Portland cement and white Portland cement, as well as rapid hardening cements and alumina cements.

As the rapid hardening cements, "Jet cement" trade name, manufactured by Onoda Cement Co., Ltd. and "Denka Super Cement" trade name, manufactured by Denki Kagaku Kogyo K.K., may be mentioned.

As the alumina cements, "Denka Alumina Cement No. 1" and "Denka Alumina Cement No. 2" trade names, manufactured by Denki Kagaku Kogyo K.K., may be mentioned.

Further, low exothermic cements such as moderate heat cement, blast furnace cement and fly ash cement as well as sulfate resistant cements, may also be used. Furthermore, if a suitable aging method is employed, calcium hydroxide or calcium oxide may also be used. Further, it is possible to use a cement material containing blast furnace slag or fly ash in a larger amount than usual blended cements. High sulfate slag cement or improved blast furnace cement may also be used.

When an alumina cement is used as the cement, it is preferred to employ as a hardening control agent one or more materials selected from the group consisting of various sulfates, nitrates and carbonates, other inorganic salts such as lithium salts and CaCl_2 , inorganic substances such as $\text{Ca}(\text{OH})_2$, borax and boric acid, and organic acids such as citric acid, tripolyphosphoric acid, pyrophosphoric acid, tartaric acid and gluconic acid and their salts.

The hardening control agent is used preferably in an amount of from 0.005 to 2 parts by weight relative to 100 parts by weight of the alumina cement.

The particle size of the cement material is usually within a range of from 5 to 30 μm . However, so long as it has a hydraulic property, the particle size may be smaller or larger than this.

Further, a rapid hardening and quick setting agent, an expansive agent, a high strength additive and various chemical additives which are commonly employed in cement concrete, may be used in combination with the cement material.

As the rapid hardening and quick setting agent, "Denka Natomic" or "Denka Cosmic" trade name, manufactured by Denki Kagaku Kogyo K.K., may be mentioned. As the expansive agent, "Denka CSA#20" trade name, manufactured by Denki Kagaku Kogyo K.K., may be mentioned. As the high strength additive, "Denka Σ -1000" trade name, manufactured by Denki Kagaku Kogyo K.K., may be employed.

In the present invention, it is effective to use inorganic ultrafine particles in combination with the cement to attain a lower water/cement ratio.

The ultrafine particles used here are particles which have an average particle size smaller by at least 1 order, preferably by 2 orders of magnitude, than the average particle size of the cement material. More preferably, their average particle size is not higher than 1 μm .

With respect to the composition of the ultrafine particles, there is no particular restriction. However, material readily soluble in water is not suitable. They may be prepared by any method such as a liquid phase method, a vapor phase method, a pulverization method or a classification method, or a combination

classification, those produced in a vapor phase as by-products such as silica dust (silica fume) obtained as by-product during the preparation of silicon, a silicon-containing alloy or zirconia, as well as fine powders such as blast furnace slag, fly ash, silica gel, opalic silica, clay mineral such as bentonite or fired products thereof, or amorphous alumina silicate. They can be prepared by means of a combination of a mill and an air separator. By the use of such ultrafine particles, freeze and fusion resistance will be improved.

Further, ultrafine powder of e.g. calcium carbonate, titanium oxide, aluminum oxide, zirconium oxide, various glass materials, chromium oxide and active carbon, may be used in combination.

The ultrafine particles may be used preferably in an amount of from 5 to 100 parts by volume, more preferably from 10 to 50 parts by volume, per 100 parts by volume of the cement material from the viewpoint of the density of the kneaded mixture and the high strength characteristics. If the amount is less than 5 parts by volume, no adequate effect for improving the density of the kneaded mixture will be obtained as compared with the case where no ultrafine particles are incorporated. On the other hand, if the amount exceeds 50 parts by weight, the abrasion resistance of the surface or the strength characteristics tend to be inadequate as compared with the case where no ultrafine particles are incorporated. In a case where only the durability attributable to the density is to be improved, a certain effect can be attained even when the amount is less than 5 parts by weight.

The ratio of the solid content of the copolymer latex to the ultrafine particles is usually within a range of from 95:5 to 5:95 by weight, preferably from 90:10 to 50:50 by weight, more preferably from 70:30 to 50:50 by weight.

When the copolymer latex is added to a hydraulic material, it sometimes happens that air bubbles are entrained, and the strength and the density of the resulting solidified product becomes low. In such a case, it is preferred to use a defoaming agent in combination.

Such defoaming agent includes an oil type defoaming agents such as sesame oil, a fatty acid type defoaming agent such as stearic acid, an alcohol type defoaming agent such as octyl alcohol, a partial ester of a polyhydric alcohol with a fatty acid such as a sorbitan fatty acid ester, polyoxyethylene polyoxypropylene ether, paraffin and a silicon type defoaming agent.

Commercial products include "TSA 732" (silicon type) trade name, manufactured by Toshiba Silicon K.K., "Kararin 302" (alcohol type) trade name, manufactured by Sanyo Kasei Kogyo K.K., "Pronal 502" (polyoxyethylene polyoxypropylene ether type) trade name, manufactured by Toho Chemical Industry Co., Ltd. and "Antiform E-20" trade name, manufactured by Kao Corporation.

Such defoaming agent is used usually in an amount of from 1 to 5 parts by weight per 100 parts by weight of the solid content of the copolymer latex.

When the cement material and the ultrafine particles are used as the cement, and a water reducing agent is used in an amount of from 1 to 3 parts by weight per 100 parts by weight of the cement, it is preferred to adjust the amount of water to a level of not higher than 45 parts by weight per 100 parts by weight of the cement in order to secure excellent fluidity. Even a water/cement ratio of not higher than 30 parts by weight is practically feasible. When the amount of water is not higher than 45 parts by weight, the strength and the density will further be improved, whereby the diffusion coefficient of chlorine ions or the water permeation coefficient will be substantially small.

The amount of water is preferably not higher than 30 parts by weight, more preferably not higher than 28 parts by weight, with a view to securing excellent fluidity.

In the present invention, it is possible to incorporate aggregates having particle sizes larger than the above mentioned various materials.

The aggregates are those having particle sizes exceeding 100 μm . As such aggregates, it is possible to use usual sand, gravel or light weight aggregates. It is of course possible to use hard aggregates selected to have a Moh's hardness of at least 6 or a Knoop indenter hardness of at least 700 kgf/mm². Further, glass or metal may also be used as aggregates.

The aggregates are used usually in an amount of up to 1,000 parts by weight per 100 parts by weight of the cement. However, the amount is not limited to such a range in the case of a special construction method such as a prepacked concrete or a post packed concrete method.

There is no particular restriction as to the method of admixing or the order of adding the above materials, so long as they can be admixed uniformly. The admixed product may be applied by injection or as a coating.

Further, in the present invention, the above materials may be combined with reinforcing materials such as iron frames or iron cores, or fibers to reinforce the tensile or flexural strength.

Examples of such fibers include metal fibers such as fibers obtained by milling cast iron, steel fibers and stainless steel fibers, various natural or synthetic mineral fibers such as asbestos, ceramic fibers,

Further, it is possible to use steel rods or molded products of alumina fibers which have been commonly used as reinforcing materials. These reinforcing materials are often required particularly for large-sized objects.

There is no particular restriction as to the aging of the kneaded product obtained by kneading the cement composition of the present invention thus obtained. However, it is preferred to conduct a wet aging at first and then a dry aging.

The kneaded product of the cement composition of the present invention thus prepared may be used for various applications including durable concrete structures or repair materials for rust-preventive coating of corroded steel bar, or for covering the peeled portions of the concrete structures, paving materials for pavements, water-preventing materials such as floor materials or roof slabs, adhesives for tiles, decorative finishing materials, floor materials for chemical plants, corrosion preventing materials such as ceiling materials for acid resistant tiles and deck covering materials.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples.

EXAMPLE 1

An ethylene (E)/vinyl acetate (VAc)/2-ethylhexyl acrylate (2EHA) copolymer latex having a composition as shown in Table 1 was prepared, and a polymer-containing cement composition was kneaded to have a blend composition as shown in Table 1. The results are shown in Table 1.

Conditions for preparing the copolymer latex

Into a stainless steel autoclave, water, VAc, 2EHA and an emulsion stabilizer were charged and heated to a temperature of 60 °C under stirring, and then ethylene was injected in a predetermined amount. Then, ammonium persulfate was added thereto to initiate the polymerization, and the polymerization was conducted until the residual monomer became not more than 0.5 part by weight. The product was cooled to obtain the copolymer latex.

Materials used

Cement:	"Onoda White Cement" trade name, manufactured by Onoda Cement Co., Ltd., specific gravity: 3.14
Ultrafine particles:	Silica fume, manufactured by Nippon Jyukagaku Kogyo K.K., average particle size: 0.2 μ m as measured by TEM, specific gravity: 2.2
Aggregate:	"Silica sand No. 7" trade name, manufactured Hisago Sangyo K.K.
Defoaming agent:	"TSA 732" trade name, manufactured by Toshiba Silicon K.K.
Water reducing agent:	"Selfro-110P" trade name, manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd., main component: a naphthalene sulphonic acid formaldehyde condensation product

Table 1

Test No.	Mortar composition (parts by weight)							Copolymer latex composition (parts by weight)					Mortar flow value (mm)	Notes
	Cement	Ultra-fine particles	Aggregate	Co-polymer latex	Defoaming agent	Water reducing agent	Water	Copolymer composition	Emulsion stabilizer composition					
									Water					
									Nonionic	PVA	HEC			
1-1	180	20	100	20	0.2	2	80	E:VAC:2EHA = 8:40:42	2.0	5.0	1.0	100	165	Comparative Example
1-2	180	20	100	20	0.2	2	80	E:VAC:2EHA = 8:40:42	8.0	0	0	100	245	Example
1-3	180	20	100	20	0.2	3	80	E:VAC:2EHA = 8:40:42	2.0	5.0	1.0	100	172	Comparative Example
1-4	180	20	100	20	0.2	3	80	E:VAC:2EHA = 8:40:42	8.0	0	0	100	> 300	Example
1-5	180	20	100	20	0.2	3	60	E:VAC:2EHA = 8:40:42	8.0	0	0	100	250	Example

Cement, ultrafine particles, aggregate, copolymer latex (calculated as solid content) and defoaming agent are presented by "parts by weight".

Water reducing agent and water are presented by "parts by weight per 100 parts by weight of the total amount of cement and ultrafine particles".

identified in Table 2. The results are shown in Table 2.

Conditions for the preparation of the copolymer latex

5 The operation was conducted in the same manner as in Example 1 except that into the stainless steel autoclave, water, VAc, 2EHA and an emulsion stabilizer were charged with a composition as identified in Table 2.

The materials used for the mortar were the same as in Example 1. However, the following was used as the water reducing agent.

10 "Melment" trade name, manufactured by Showa Denko K.K., main component: a salt of a melamine sulphonic acid formaldehyde condensation product

Emulsion Stabilizer: Nonionic surfactant; "Emulgen 985" trade name, manufactured by Kao Corporation, main component: polyoxyethylene alkylphenyl ether HLB = 18.9

PVA: "Denkapoval B-17" trade name, manufactured by Denki Kagaku Kogyo K.K.

15 HEC: "AH-15" trade name, manufactured by Fuji Chemical K.K.

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Table 2

Test No.	Mortar composition (parts by weight)						Copolymer latex composition (parts by weight)						Mortar flow value (mm)	Notes	Adhesive strength (kgf/cm ²)	Compression strength (kgf/cm ²)
	Cement	Ultra-fine particles	Aggregate	Co-polymer latex	Defoaming agent	Water reducing agent	Water	Copolymer composition	Emulsion, stabilizer composition			Water				
									Nonionic	PVA	HEC					
2-1	180	20	100	20	0.2	2	70	E:VAC:2EHA = 8:46:46	8.0	0	0	100	Example	57	490	
2-2	180	20	100	20	0.2	2	70	E:VAC:2EHA = 18:82:0	8.0	0	0	100	Comparative Example	59	490	
2-3	180	20	100	20	0.2	3	70	E:VAC:2EHA = 16:67:17	8.0	0	0	100	Comparative Example	56	500	
2-4	180	20	100	20	0.2	3	70	E:VAC:2EHA = 18:2:80	8.0	0	0	100	Example	54	485	
2-5	180	20	100	20	0.2	3	60	E:VAC:2EHA = 18:2:80	8.0	0	0	100	Example	55	480	
2-6	200	0	100	20	0.2	2	70	E:VAC:2EHA = 8:46:46	8.0	0	0	100	Example	50	470	
2-7	200	0	100	20	0.2	3	70	E:VAC:2EHA = 8:46:46	8.0	0	0	100	Example	51	475	
2-8	180	20	100	20	0.2	3	70	E:VAC:2EHA = 8:46:46	8.0	0	0	100	Example	54	480	
2-9	180	20	100	20	0.2	3	70	E:VAC:2EHA = 18:2:80	8.0	0	0	100	Example	53	475	

Test Nos. 2-1 to 2-5: Water reducing agent was "Selflow-110P" manufactured by Daiichi Kogyo Seiyaku.

Test Nos. 2-7 to 2-9: Water reducing agent was "Melment".

EXAMPLE 3 (Comparison in the freeze and fusion resistance between ultrafine particles + EVA and EVA)

Using a blend composition as identified in Table 3 and a polymer-containing cement mortar adjusted to bring the cement/sand ratio to 1/3 and the mortar slump to 35±5 mm, a test for freezing and fusing was

Table 3 (Parts by weight)

Test No.	Cement	Silica sand	Water	Water reducing agent	Ultra-fine particles	Co-polymer latex
3-1	100	300	61	0	0	A10
3-2	100	300	45	1.0	0	B10
3-3	90	300	35	1.0	10	B10

Materials used

- Cement: Normal Portland cement, manufactured by Denki Kagaku Kogyo K.K.
 Silica sand: "Silica sand No. 6" manufactured by Tohoku Kaisha K.K.
 Water: City water
 Copolymer latex A: Ethylene-vinyl acetate copolymer manufactured by Denki Kagaku Kogyo K.K. (added in an amount calculated as solid content).
 Copolymer latex B: A modified acryl-ethylene-vinyl acetate copolymer, manufactured by Denki Kagaku Kogyo K.K. (added as calculated as solid content).

Table 3' (Relative dynamic elastic modulus)

No.	Number of cycles*1	0	30	60	90	120	150	180	210	240	270	300
		% 100	103	100	104	99	80	64	60 or less	-	-	-
1		% 100	103	100	104	99	80	64	60 or less	-	-	-
2		% 100	101	100	98	95	85	80	76	72	67	60
3		% 100	100	100	102	104	97	100	98	100	101	102

*1: Number of cycles of freezing and fusing

The test was conducted in accordance with ASTM C-666 method A (freezing in water and fusing in water).

The "durability factor DF" according to the same test method is represented by:

$$DF = \frac{P \cdot N}{N_s} (\%)$$

P: Relative elastic modulus at N cycle (%)

N: Number of the cycles at the end of the test

Ns: Prescribed number of cycles (=300 cycles)

In test No. 1,

$$DF = \frac{60 \cdot 210}{300} = 42\%$$

In test No. 2,

$$DF = \frac{60 \cdot 300}{300} = 60\%$$

In test No. 3,

$$DF = \frac{102 \cdot 300}{300} = 102\% = 100\%$$

The cement admixture and the polymer cement composition of the present invention provide excellent compression strength and adhesive strength without impairing fluidity even when the water/cement ratio is lowered, and they are effective for improving the density and the durability.

Claims

1. A cement admixture comprising a polymer latex, ultrafine particles having an average particle size smaller by at least one order of magnitude than the average particle size of the cement material, and a water-reducing agent as effective components, wherein the polymer latex comprises a copolymer of monomers comprising ethylene, vinyl acetate and acrylic ester and an emulsion stabilizer, wherein said emulsion stabilizer is a surfactant in the absence of a colloid.
2. The cement admixture according to Claim 1, wherein said copolymer is a copolymer of monomers comprising from 3 to 25 parts by weight of ethylene, from 2 to 60 parts by weight of vinyl acetate, from 25 to 85 parts by weight of an acrylic ester and from 0 to 10 parts by weight of other copolymerizable monomers.
3. The cement admixture according to Claim 1, wherein the water reducing agent is a melamine resin sulfonate.
4. The cement admixture according to Claim 1, wherein the water reducing agent is at least one member selected from the group consisting of a salt of a naphthalene sulfonic acid formaldehyde condensation product, a salt of an alkylnaphthalene sulfonic acid formaldehyde condensation product, a lignin sulfonate and a polystyrene sulfonate.
5. The cement admixture according to Claim 1, wherein the ultrafine particles are at least one member

pulverized product of fly ash.

6. The cement admixture according to Claim 1, wherein the ratio of the solid content of the copolymer latex to the water reducing agent is within a range of from 98:2 to 10:90 by weight.
7. The cement admixture according to Claim 1, wherein the ratio of the solid content of the copolymer latex to the ultrafine particles is within a range of from 95:5 to 5:95 by weight.
8. A cement composition comprising cement and the cement admixture of Claim 1.
9. A cement composition comprising cement and the cement admixture of Claim 4 or 5.

Patentansprüche

1. Zement-Beimischung, umfassend eine Polymerlatex, ultrafeine Teilchen mit einer mittleren Teilchengröße, die mindestens eine Größenordnung kleiner ist, als die mittlere Teilchengröße des Zementmaterials und ein wasserverminderndes Mittel als wirksame Bestandteile, worin die Polymerlatex ein Copolymer von Monomeren umfaßt, die Ethylen, Vinylacetat und Acrylester umfassen, sowie einen Emulsions-Stabilisator, wobei der Emulsions-Stabilisator in Abwesenheit eines Kolloids ein oberflächenaktives Mittel ist.
2. Zement-Beimischung nach Anspruch 1, worin das Copolymer ein Copolymer von Monomeren ist, die von 3 bis 25 Gewichtsteile Ethylen, von 2 bis 60 Gewichtsteile Vinylacetat, von 25 bis 85 Gewichtsteile eines Acrylesters und von 0 bis 10 Gewichtsteile anderer copolymerisierbarer Monomeren umfassen.
3. Zement-Beimischung nach Anspruch 1, worin das wasservermindernde Mittel ein Melaminharzsulfonat ist.
4. Zement-Beimischung nach Anspruch 1, worin das wasservermindernde Mittel mindestens eines ist, ausgewählt aus der Gruppe bestehend aus einem Salz eines Naphthalinsulfonsäure-Formaldehyd-Kondensationsproduktes, einem Salz eines Alkyl-naphthalinsulfonsäure-Formaldehyd-Kondensationsproduktes, einem Ligninsulfonat und einem Polystyrolsulfonat.
5. Zement-Beimischung nach Anspruch 1, worin die ultrafeinen Teilchen mindestens eines, ausgewählt aus der Gruppe bestehend aus pyrogenem Siliciumdioxid, einem pulverisierten Produkt von Hochofenschlacke und einem pulverisierten Produkt von Flugasche sind.
6. Zement-Beimischung nach Anspruch 1, worin das Verhältnis des Feststoffgehaltes der Copolymerlatex zum wasservermindernden Mittel innerhalb eines Bereiches von 98:2 bis 10:90, bezogen auf das Gewicht, liegt.
7. Zement-Beimischung nach Anspruch 1, worin das Verhältnis des Feststoffgehaltes der Copolymerlatex zu den ultrafeinen Teilchen innerhalb eines Bereiches von 95:5 bis 5:95, bezogen auf das Gewicht, liegt.
8. Zement-Zusammensetzung, umfassend Zement und die Zement-Beimischung nach Anspruch 1.
9. Zement-Zusammensetzung, umfassend Zement und die Zement-Beimischung nach Anspruch 4 oder 5.

Revendications

1. Additif pour ciment comprenant un latex polymère, des particules ultrafines ayant une dimension moyenne de particule inférieure d'au moins un ordre de grandeur à la dimension moyenne de particule du matériau formant ciment, et un agent de réduction de la teneur en eau comme composants actifs, additif dans lequel le latex polymère comprend un copolymère de monomères comprenant l'éthylène, l'acétate de vinyle et un ester acrylique ainsi qu'un stabilisateur d'émulsion, ledit stabilisateur d'émul-

2. Additif pour ciment selon la revendication 1, dans lequel ledit copolymère est un copolymère de monomères comprenant 3 à 25 parties en poids d'éthylène, 2 à 60 parties en poids d'acétate de vinyle, 25 à 85 parties en poids d'un ester acrylique et 0 à 10 parties en poids d'autres monomères copolymérisables.
3. Additif pour ciment selon la revendication 1, dans lequel l'agent de réduction de la teneur en eau est un sulfonate de résine mélamine.
4. Additif pour ciment selon la revendication 1, dans lequel l'agent de réduction de la teneur en eau est au moins un élément choisi dans le groupe constitué d'un sel d'un produit de condensation d'acide naphthalène sulfonique et de formaldéhyde, d'un sel d'un produit de condensation d'acide alkylnaphtalène sulfonique et de formaldéhyde, d'un sulfonate de lignine et d'un sulfonate de polystyrène.
5. Additif pour ciment selon la revendication 1, dans lequel les particules ultrafines sont constituées d'au moins un élément choisi parmi la fumée de silice, un produit pulvérisé formé de laitier de haut-fourneau et un produit pulvérisé de cendres volantes.
6. Additif pour ciment selon la revendication 1, dans lequel le rapport de la teneur en solides du latex copolymère à l'agent de réduction de la teneur en eau se situe dans la plage de 98:2 à 10:90 en poids.
7. Additif pour ciment selon la revendication 1, dans lequel le rapport de la teneur en solides du latex copolymère aux particules ultrafines se situe dans la plage de 95:5 à 5:95 en poids.
8. Composition de ciment comprenant du ciment et l'additif pour ciment de la revendication 1.
9. Composition de ciment comprenant du ciment et l'additif pour ciment de la revendication 4 ou 5.